

Modeling the Thermodynamic Properties of Solutions Containing Polymer and Electrolyte with New Local Composition Model

A. Mohammadian-Abriz^{a,b} and R. Majdan-Cegincara^{b,*}

^aDepartment of Chemical Engineering, East Azarbaijan Science and Research Branch, Islamic Azad University, Tabriz, Iran

^bDepartment of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran

(Received 6 January 2017, Accepted 9 April 2017)

A new model based on the local composition concept (TNRF-modified NRTL (TNRF-mNRTL) model) was developed to express the short-range contribution of the excess Gibbs energy for the solutions containing polymer and electrolyte. An equation represented the activity coefficient of solvent was derived from the proposed excess Gibbs energy equation. The short-range contribution of interaction along with the long-range contribution of interaction and configurational entropy of mixing were used to correlate the activity coefficient of ternary polymer + electrolyte + water systems and also binary polymer + water and electrolyte + water systems. The long-range interaction and configurational entropy were given by the Pitzer-Debye-Hückel equation and the Flory-Huggins relation, respectively. The performance of the proposed model in fitting the solvent activity of ternary polymer + electrolyte + water solutions was compared with that obtained from the ternary NRTL, ternary Wilson, ternary modified NRTL and ternary modified Wilson models. Results comparison demonstrated the validity of the proposed model for solvent activity of polymer + electrolyte + water solutions.

Keywords: Mathematical modeling, Aqueous solutions of polymer + electrolyte, Thermodynamic properties, TNRF-mNRTL model, Activity coefficient

INTRODUCTION

Fast, cost-effective and ecofriendly method of aqueous two-phase system consisting of a polymer and one kosmotropic salt has a great potential for development in biotechnology applications as separation media and purification of enzyme, drugs, macromolecules, metal ions and biomaterials [1-3]. This simple system can also be used in protein partitioning to obtain the enriched products [1,4]. The knowledge of measurement, correlation and prediction of the thermodynamic, transport and volumetric properties of polymer + electrolyte solutions is necessary for designing and operating the industrial processes. Various models have been proposed for correlation of the thermodynamic properties of aqueous two phase systems based on the osmotic virial expansions [5,6] or the local composition

concept [7-10]. Measurement and modeling the water activity in the aqueous two-phase systems have particular importance in view point of industrial applications. The local composition models are a matter of interest because of their simplicity and accuracy in correlating the vapor liquid equilibrium (VLE) data. The NRTL local composition model was extended by Zafarani-Moattar and Sadeghi [7] to represent the excess Gibbs energy of aqueous polymer + electrolyte solutions. The Wilson model has also been extended [8] to describe the experimental VLE data of aqueous polymer + electrolyte solutions. Sadeghi proposed the modified NRTL [9] and the modified Wilson [10] models for correlating the VLE data of the aqueous polymer + electrolyte solutions.

In spite of developing several local composition models for modeling the thermodynamic properties of the systems containing polymer and electrolyte, number of models with high precision is scarce. Local composition models can be

*Corresponding author. E-mail: majdan@iaut.ac.ir

easily extended for the multicomponent systems, therefore, we decided to develop a new excess Gibbs energy model based on local composition concept using Chen's local cell theory [11]. New relations were used for the reference states of four types of local cells in derivation of the proposed model. This model, which is a TNRF-modified NRTL (TNRF-mNRTL) model, is developed for representing the short range contribution of excess Gibbs energy of the solutions containing polymer and electrolyte. This model along with the configurational entropy of mixing and the long-range contribution of interaction are used to correlate the thermodynamic properties of the ternary solutions of polymer + electrolyte + water and binary solutions of polymer + water and electrolyte + water. The configurational entropy of mixing and the long-range contribution of interaction are represented by the Flory-Huggins relation [12] and the Pitzer-Debye-Hückel model [13], respectively. The performance of the proposed model in correlating the solvent activity of ternary polymer + electrolyte + water solutions is compared with that obtained from the models which are available in the literature for these systems; ternary NRTL [7], ternary Wilson [8], ternary modified NRTL [9] and ternary modified Wilson [10] models.

THEORETICAL FRAMEWORK

New Excess Gibbs Energy Equation

Chen et al. assumed the existence of three and two types of cells, depending on the central species, respectively, in the development of the electrolyte-NRTL [11] and polymer-NRTL models [14]. Following the Chen et al.'s approach, we assumed the existence of the four types of cells for expression the local physical interactions between solvent (m), segment of polymer chains (s), anion (a) and cation (c) in polymer + electrolyte solutions, as shown in Fig. 1. One of the cells has a polymer segment as a central molecule with solvent, segment, anion and cation molecules in the surrounding (Fig. 1a) and the second cell has a solvent as a central molecule with solvent, polymer segment, anion and cation molecules in the surrounding (Fig. 1b) and the third cell has an anion as a central molecule with solvent, polymer segment, and cation

molecules in the surrounding (Fig. 1c) and the fourth cell has a cation as a central molecule with solvent, polymer segment and anion molecules in the surrounding (Fig. 1d). Thus, the excess Gibbs energy (g^{ex}) can be obtained with considering the contribution of the excess Gibbs energy of each cell (g_m^{ex} , g_a^{ex} , g_c^{ex} and g_s^{ex}) as follows:

$$\frac{g^{ex, TNRF-mNRTL}}{RT} = x_m \frac{g_m^{ex}}{RT} + x_a \frac{g_a^{ex}}{RT} + x_c \frac{g_c^{ex}}{RT} + r_p x_p \frac{g_s^{ex}}{RT} \quad (1)$$

where x_m , x_a , x_c and x_p are the mole fraction of solvent, anion, cation and polymer. The number of polymer segments, r_p , approximates the ratio of the molar volume of the polymer and that of the solvent molecules. T is temperature and R is the universal constant of gases. Subscripts m , a , c and s represent the solvent, anion, cation and segment of polymer chain, respectively. The contributions of the excess Gibbs energy for the four cells are defined as [11,14]

$$g_m^{ex} = (X_{mm} g_{mm} + X_{cm} g_{cm} + X_{am} g_{am} + X_{sm} g_{sm}) - g_m^0 \quad (2a)$$

$$g_a^{ex} = (X_{ma} g_{ma} + X_{ca} g_{ca} + X_{sa} g_{sa}) - g_a^0 \quad (2b)$$

$$g_c^{ex} = (X_{mc} g_{mc} + X_{ac} g_{ac} + X_{sc} g_{sc}) - g_c^0 \quad (2c)$$

$$g_s^{ex} = (X_{ms} g_{ms} + X_{as} g_{as} + X_{cs} g_{cs} + X_{ss} g_{ss}) - g_s^0 \quad (2d)$$

where g_m^0 , g_a^0 , g_c^0 and g_s^0 are the reference states Gibbs energy for the cells with central solvent, anion, cation and segment, respectively. G_{ji} and g_{ii} are the energies of interaction between j-I and i-I pairs of species, respectively. X_{ji} and X_{ii} are the effective local mole fractions of species j and i.

In this work, the new relations were used for the reference states of four types of cells, as follows:

$$g_m^0 = X_m g_{mm} + X_a g_{am} + X_c g_{cm} + X_s g_{sm} \quad (3a)$$

$$g_a^0 = \frac{X_c g_{ca} + X_m g_{ma} + X_s g_{sa}}{X_c + X_m + X_s} \quad (3b)$$

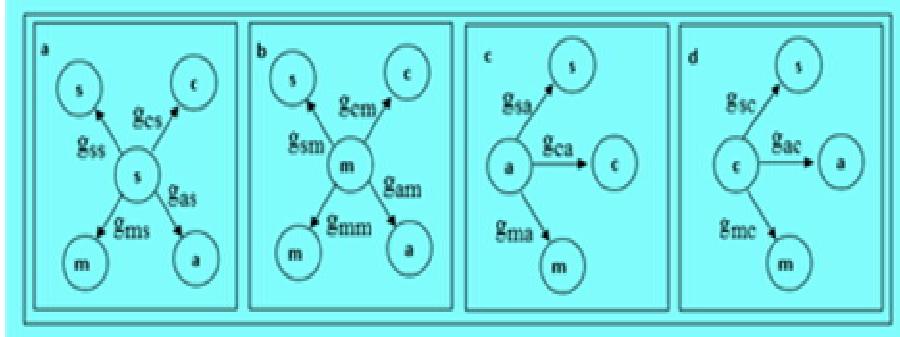


Fig. 1. Four types of cells for expression the local physical interactions between solvent (m), segment of polymer chains (s), anion (a) and cation (c) in aqueous polymer + electrolyte solutions depending on central species.

$$g_c^0 = \frac{X_a g_{ac} + X_m g_{mc} + X_s g_{sc}}{X_a + X_m + X_s} \quad (3c)$$

$$g_s^0 = \frac{X_m g_{ms} + X_a g_{as} + X_c g_{cs} + X_s g_{ss}}{X_m + X_a + X_c + X_s} \quad (3d)$$

Where

$$X_a = z_a x_a = X_E = z_a z_c x_h \quad (4a)$$

$$X_c = z_c x_c = X_E = z_a z_c x_h \quad (4b)$$

$$X_m = x_m \quad (4c)$$

$$X_s = \frac{x_p}{r_p x_p + x_m + 2z_a z_c x_h} \quad (4d)$$

here, z_a and z_c are the charge number of anion and cation, respectively. From Eqs. (4a) and (4b) we have the relation $X_a = X_c$ which shows the electroneutrality.

Using the nonrandom factor same as that defined by Haghtalab and Vera. [15] and considering the above assumptions by following the same procedure as our previous works [16,17] used, respectively, in obtaining the excess Gibbs energy expression for electrolyte solutions and polymer solutions, we obtained the TNRF-mNRTL equation for unsymmetrical convention ($g^{ex*,TNRF-mNRTL}$) as follows:

$$\frac{g^{ex*,TNRF-mNRTL}}{RT} = x_m [\lambda_{mEm} (x_m \Gamma_m - x_m) + \lambda_{sm} (X_s \Gamma_s - X_s)] + \frac{z_a z_c x_h}{z_a + z_c} \left[\frac{z_a z_c x_h \lambda_{mE} (-1 + z_a z_c x_h \Gamma_E + x_m \Gamma_E + X_s \Gamma_E) + X_s \lambda_{Es} (z_a z_c x_h \Gamma_s + X_s \Gamma_s + X_m \Gamma_s - 1)}{X_E + x_m + X_s} \right] + r_p x_p \left[\frac{2z_a z_c x_h \lambda_{sE} (\Gamma_E - 1) + X_s \lambda_{ms} (\Gamma_s - 1)}{x_m + X_s + 2z_a z_c x_h} \right] - \nu x_h \lambda_{Em} (1 - \Gamma_m) \quad (5a)$$

Where

$$\frac{g_{ca} - g_{ma}}{RT} \equiv \lambda_{mE}, \quad \frac{g_{mm} - g_{Em}}{RT} \equiv \lambda_{Em} \quad (5b)$$

$$\frac{g_{sa} - g_{ma}}{RT} \equiv \lambda_{Es}, \quad \frac{g_{Es} - g_{ms}}{RT} \equiv \lambda_{sE} \quad (5c)$$

$$\frac{g_{sm} - g_{Em}}{RT} \equiv \lambda_{sm}, \quad \frac{g_{ss} - g_{ms}}{RT} \equiv \lambda_{ms} \quad (5d)$$

$$\Gamma_s = \frac{1}{2z_a z_c x_h \beta_{Es} + x_m \beta_{ms} + X_s}, \quad \beta_{Es} = \exp\left(-\frac{\lambda_{Es}}{Z}\right) \\ \beta_{ms} = \exp\left(-\frac{\lambda_{ms}}{Z}\right) \quad (5e)$$

$$\Gamma_m = \frac{1}{2z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm}}, \quad \beta_{Em} = \exp\left(-\frac{\lambda_{Em}}{Z}\right) \\ \beta_{sm} = \exp\left(-\frac{\lambda_{sm}}{Z}\right) \quad (5f)$$

$$\Gamma_E = \frac{\beta_{mE}}{z_a z_c x_h \beta_{mE} + x_m + X_s \beta_{sE}}, \quad \beta_{mE} = \exp\left(-\frac{\lambda_{mE}}{Z}\right) \\ \beta_{sE} = \exp\left(-\frac{\lambda_{sE}}{Z}\right) \quad (5g)$$

where $x_h = 1 - x_m - x_p$, and $\lambda_{mE}, \lambda_{Em}, \lambda_{sE}, \lambda_{Es}, \lambda_{sm}$ and λ_{ms} are the adjustable parameters of TNRF-mNRTL model, Z is the nonrandom factor which was set to 8 for obtaining the better quality of fitting in this work, and $v = v_c + v_a$, where v_c and v_a are the stoichiometric coefficients of cation and anion, respectively.

Activity Coefficient Equation

The activity coefficient equation of the solvent for the short-range contribution of interaction can be derived from the Eq. (5) using the following relation [13]

$$\ln \gamma_m^* = \frac{\partial}{\partial n_m} \left(\frac{n g^{ex*}}{RT} \right) \quad (6)$$

where n and n_m are the total mole number and the mole number of solvent, respectively. The derived activity coefficient equation of the solvent for TNRF-mNRTL model is as follows:

$$\begin{aligned} \ln \gamma_m^{*,TNRF-mNRTL} = & \lambda_{Em} x_m Q_1 + \lambda_{sm} x_m Q_1 + x_m (\lambda_{Em} Q_1 - \lambda_{Em} x_m Q_1 - \lambda_{Em} x_m Q_2 - \lambda_{sm} x_s Q_1 \\ & - \lambda_{sm} x_s Q_3 - \lambda_{sm} x_s Q_2) + \frac{z_a z_c x_h}{(z_a + z_c)(z_a z_c x_h + x_m + X_s)} [-\lambda_{mE} z_a z_c x_h (-1 + Q_4 z_a z_c x_h + x_m Q_4 \\ & + x_s Q_4) + \lambda_{mE} z_a z_c x_h (-Q_4 z_a z_c x_h - Q_5 z_a z_c x_h \beta_{mE} + Q_4 - x_m Q_4 - x_m \beta_{mE} Q_5 - x_s Q_4 - x_s Q_3 Q_4 \\ & - x_s \beta_{mE} Q_5) - \lambda_{Es} X_s (Q_6 z_a z_c x_h + X_s Q_6 + X_m Q_6 - 1) - \lambda_{Es} X_s Q_3 (Q_6 z_a z_c x_h + X_s Q_6 + X_m Q_6 - 1) \\ & + \lambda_{Es} X_s (-Q_6 z_a z_c x_h - Q_7 z_a z_c x_h - X_s Q_6 - X_s Q_3 Q_6 - X_s Q_7 + Q_6 - X_m Q_6 - X_m Q_7)] \\ & - \frac{z_a z_c x_h}{(z_a + z_c)(z_a z_c x_h + x_m + X_s)} [\lambda_{mE} z_a z_c x_h (-1 + Q_4 z_a z_c x_h + x_m Q_4 + x_s Q_4) + \lambda_{Es} X_s (Q_6 z_a z_c x_h \\ & - X_s Q_6 + x_m Q_6 - 1)(z_a z_c x_h - 1 + x_m - X_s - X_s Q_3)] + \frac{r p^x p}{2 z_a z_c x_h + x_m + X_s} [-2 \lambda_{sE} z_a z_c x_h (Q_4 - 1) \\ & - 2 \lambda_{sE} Q_5 z_a z_c x_h \beta_{mE} - \lambda_{ms} X_s (Q_6 - 1) - \lambda_{ms} X_s (Q_6 - 1) Q_3 - \lambda_{ms} X_s Q_7] \\ & - \frac{r p^x p}{(2 z_a z_c x_h + x_m + X_s)^2} [2 \lambda_{sE} z_a z_c x_h (Q_4 - 1) + \lambda_{ms} X_s (Q_6 - 1)] (1 - x_m - 2 z_a z_c x_h - X_s - X_s z_a z_c x_h) \end{aligned} \quad (7a)$$

where

$$Q_1 = \frac{1}{2 z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm}} - 1 \quad (7b)$$

$$Q_2 = \frac{-2 z_a z_c x_h \beta_{Em} + 1 - x_m - X_s \beta_{sm} - X_s \beta_{sm} \left(\frac{1 - x_m - r p^x p^{-x_h}}{x_m + r p^x p^{-x_h}} \right)}{(2 z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm})^2} \quad (7c)$$

$$Q_3 = \frac{1 - x_m - r p^x p^{-x_h}}{x_m + r p^x p^{-x_h}} \quad (7d)$$

$$Q_4 = \frac{\beta_{mE}}{z_a z_c x_h \beta_{mE} + x_m + X_s \beta_{sE}} \quad (7e)$$

$$Q_5 = \frac{-z_a z_c x_h \beta_{mE} + 1 - x_m - X_s \beta_{sE} - X_s \beta_{sE} \left(\frac{1 - x_m - r p^x p^{-x_h}}{x_m + r p^x p^{-x_h}} \right)}{(z_a z_c x_h \beta_{Em} + x_m + X_s \beta_{sm})^2} \quad (7f)$$

$$Q_6 = \frac{1}{2 z_a z_c x_h \beta_{Es} + x_m \beta_{ms} + X_s} \quad (7g)$$

$$Q_7 = \frac{-2 z_a z_c x_h \beta_{Es} + \beta_{ms} - x_m \beta_{ms} - X_s - X_s \left(\frac{1 - x_m - r p^x p^{-x_h}}{x_m + r p^x p^{-x_h}} \right)}{(2 z_a z_c x_h \beta_{Es} + x_m \beta_{ms} + X_s)^2} \quad (7h)$$

RESULTS AND DISCUSSION

The solvent activity (a_m) for the ternary polymer + electrolyte + water solutions can be correlated with the following relation

$$\ln a_m = \ln \gamma_m + \ln x_m \quad (8)$$

The solvent activity coefficient (γ_m) for a polymer + electrolyte + water solution is defined as the sum of three contributions

$$\ln \gamma_m = \ln \gamma_m^{PDH} + \ln \gamma_m^{F-H} + \ln \gamma_m^{TNRF-mNRTL} \quad (9)$$

The Flory-Huggins relation [12] and the Pitzer-Debye-Hückel equation [13] for the activity coefficient of the solvent are as Eqs. (10) and (11), respectively

$$\ln \gamma_m^{F-H} = \ln \left(\frac{X_m}{x_m} \right) + 1 - \sum_j \frac{X_j}{r_j} \quad (10)$$

$$\ln \gamma_m^{*PDH} = \frac{2 A_\phi I_x^{1.5}}{M_m^{0.5} (1 + \rho I_x^{0.5})} \quad (11)$$

Table 1. Two Adjustable Parameters of TNRF-mNRTL Model (Eq. (7)) Along with Absolute Average Relative Deviations (100.AARD)^a Obtained from Correlating the Solvent Activity (a_m) of Ternary Aqueous Polymer + Electrolyte Solutions at 298.15 K

System	Polymer M_n	N	Concentration range (w/w) ^b	λ_{Em}	λ_{mE}	λ_{sm}	λ_{ms}	λ_{sE}	λ_{Es}	100.AARD	Source data
PEG1000 + (NH ₄) ₂ SO ₄ + H ₂ O	1000	20	0.00-0.40 0.00-0.15					-1.211	-7.568	0.11	[19]
PEG4000 + (NH ₄) ₂ SO ₄ + H ₂ O	3800	20	0.00-0.40 0.00-0.15					-0.753	-50.343	0.12	[19]
PEG6000 + (NH ₄) ₂ SO ₄ + H ₂ O	6000	24	0.00-0.41 0.00-0.10					-3.326	-61.149	0.15	[20]
PEG10000 + (NH ₄) ₂ SO ₄ + H ₂ O	9000	15	0.00-0.30 0.00-0.04					7.442	-5678.000	0.17	[21]
PEG1000 + MgSO ₄ + H ₂ O	1000	15	0.00-0.34 0.00-0.15					-3.856	-1632.000	0.26	[19]
PEG4000 + MgSO ₄ + H ₂ O	3800	15	0.00-0.34 0.00-0.11					-2.928	-5538.000	0.18	[19]
PEG8000 + MgSO ₄ + H ₂ O	6400	20	0.00-0.31 0.00-0.09					-0.737	-5678.000	0.47	[22]
PEG10000 + MgSO ₄ + H ₂ O	9000	10	0.00-0.16 0.00-0.12					-1.547	6087.000	0.08	[21]
PEG1000 + Na ₂ SO ₄ + H ₂ O	980	20	0.00-0.37 0.00-0.12					-1.437	-10.229	0.10	[22]

Table 1. Continued

PEG8000 +								
Na ₂ SO ₄ +			0.00-0.37					
H ₂ O	6400	20	0.00-0.09		0.762	-1633.000	0.06	[22]
PEG1000 +								
Na ₂ CO ₃ +			0.00-0.35					
H ₂ O	980	20	0.00-0.08		-2.100	-10.163	0.08	[22]
PEG8000 +								
Na ₂ CO ₃ +			0.00-0.36					
H ₂ O	6400	20	0.00-0.06		1.358	-2261.000	0.06	[22]
PEG4000 +								
KH ₂ PO ₄ +			0.00-0.32					
H ₂ O	3800	24	0.00-0.08		-1.906	29.426	0.09	[21]
PEG10000 +								
KH ₂ PO ₄ +			0.00-0.32					
H ₂ O	9000	24	0.00-0.11		-1.687	-1628.000	0.06	[21]
PEG4000 +								
K ₂ HPO ₄ +			0.00-0.30					
H ₂ O	3800	24	0.00-0.06		42.888	-5678.000	0.05	[21]
PEG10000 +								
K ₂ HPO ₄ +			0.00-0.37					
H ₂ O	9000	30	0.00-0.14		0.018	-3111.000	0.07	[21]
PPG425 +								
(NH ₄) ₂ SO ₄ +			0.00-0.69					
H ₂ O	404	36	0.00-0.19		-0.955	114.144	0.16	[23]
PPG425 +								
MgSO ₄ +			0.00-0.43					
H ₂ O	404	32	0.00-0.14		-10.315	-1079.000	0.69	[24]
PPG425 +								
Na ₂ SO ₄ +			0.00-0.60					
H ₂ O	404	40	0.00-0.16		-0.166	-19.852	0.16	[23]
PEG1000 +								
H ₂ O	1000	7	0.0493-0.4929	6.654	-16.571		0.45	[24]
PEG4000 +								
H ₂ O	4000	7	0.0497-0.4964	7.593	-47.677		0.38	[24]

Table 1. Continued

PEG6000 +							
H ₂ O	6000	7	0.0497-0.497		11.235	-21.966	0.05 [24]
PEG8000 +							
H ₂ O	8000	7	0.0499-0.4984		7.824	-110.964	0.42 [24]
PEG10000 +							
H ₂ O	10000	7	0.0497-0.4967		7.855	-139.194	0.41 [24]
PPG425 +							
H ₂ O	404	8	0.1828-0.4261		-8.299	-3.613	0.04 [25]
(NH ₄) ₂ SO ₄ +							
H ₂ O		22	0.100-5.500 ^c	-0.615	3.125		0.02 [26]
MgSO ₄ +							
H ₂ O		17	0.100-3.000 ^c	11.063	-5.105		0.25 [26]
Na ₂ SO ₄ +							
H ₂ O		31	0.001-1.750 ^c	-0.387	2.585		0.003 [27]
Na ₂ CO ₃ +							
H ₂ O		35	0.001-2.750 ^c	-0.621	2.352		0.03 [27]
KH ₂ PO ₄ +							
H ₂ O		20	0.001-1.800 ^c	-0.95	2.126×10 ⁻³		0.002 [28]
K ₂ HPO ₄ +							
H ₂ O		27	0.001-0.873 ^c	-0.0089	1.055		0.002 [27]

^a $AARD = \frac{\sum_{i=1}^N \left| \frac{a_{m,i}^{\text{exp}} - a_{m,i}^{\text{cal}}}{a_{m,i}^{\text{exp}}} \right|}{N}$ in which, N is the total number of data. ^bThe concentration ranges for the polymer and the salt have been

given respectively above and below in each cell of column. ^cMolality ranges of salts have been given.

where the Debye-Hückel constant for osmotic coefficient (A_ϕ) is represented as:

$$A_\phi = \frac{1}{3} (2\pi N_A d_m)^{1/2} \left(\frac{e^2}{4\pi\epsilon D_m kT} \right)^{3/2} \quad (12)$$

A_ϕ at 298.15 K is equal to 0.390947 for water as solvent. M_m and d_m are the molar mass and density of the solvent, respectively. N_A , k , ϵ , D_m and e are the Avogadro's number, Boltzmann constant, permittivity of vacuum, dielectric constant of pure solvent and electronic charge, respectively. ρ is the closest distance parameter and the value of 14.9 is commonly applied for aqueous electrolyte solutions [18]. Therefore, we used this value for ρ in our work. I_x is the

ionic strength in mole fraction basis, $I_x = 0.5 \sum_i x_i z_i^2$, z_i is the charge number of ion i . Subscript i shows the component i .

The solvent activities of the ternary solutions have successfully been correlated using the Eqs. ((7)-(12)) by minimizing the following objective function

$$OF = \sum_i (\ln(a_{m,i}^{\text{exp}}) - \ln(a_{m,i}^{\text{cal}}))^2 \quad (13)$$

where superscript exp and cal denote the experimental and calculated values, respectively. At first, the solvent activities of ternary solutions were correlated with TNRF-mNRTL model with only two adjustable parameters. The obtained

Table 2. Six Adjustable Parameters of TNRF-mNRTL Model (Eq. (7)) Along with Absolute Average Relative Deviations (100.AARD)^a Obtained from Correlating the Solvent Activity (a_m) of Ternary Aqueous Polymer + Electrolyte Solutions at 298.15 K

System	Polymer M_n	N	Concentration range (w/w)	λ_{Em}	λ_{mE}	λ_{sm}	λ_{ms}	λ_{sE}	$10^3 \lambda_{Es}$	100.AARD	Source data
PEG1000 +			0.00-0.40								
(NH ₄) ₂ SO ₄ + H ₂ O	1000	20	0.00-0.15	-1.166	7.591	-28.493	-53.445	-1.678	0.5624	0.05	[19]
PEG4000 +			0.00-0.40								
(NH ₄) ₂ SO ₄ + H ₂ O	3800	20	0.00-0.15	-0.154	3.028	-48.965	-112.227	-1.990	0.5625	0.02	[19]
PEG6000 +			0.00-0.41								
(NH ₄) ₂ SO ₄ + H ₂ O	6000	24	0.00-0.10	0.088	0.402	-172.201	-797.324	-2.037	2.250	0.01	[20]
PEG10000 +			0.00-0.30								
(NH ₄) ₂ SO ₄ + H ₂ O	9000	15	0.00-0.04	-0.450	9.768×10 ⁻⁵	-16.54	-1181.00	-15.544	-0.01395	0.02	[21]
PEG1000 +			0.00-0.34								
MgSO ₄ + H ₂ O	1000	15	0.00-0.15	2.851	0.401	-3.355	-104.636	1.508	2.250	0.05	[19]
PEG4000 +			0.00-0.34								
MgSO ₄ + H ₂ O	3800	15	0.00-0.11	-0.00314	2.124	-83.961	-120.011	-2.371	2.250	0.04	[19]
PEG8000 +			0.00-0.31								
MgSO ₄ + H ₂ O	6400	20	0.00-0.09	57.846	-1355.000	-79.962	0.784	0.479	3052.000	0.02	[22]
PEG10000 +			0.00-0.16								
MgSO ₄ + H ₂ O	9000	10	0.00-0.12	0.216	0.431	-493.578	930.723	-39.674	2.250	0.01	[21]
PEG1000 +			0.00-0.37								
Na ₂ SO ₄ + H ₂ O	980	20	0.00-0.12	-0.877	2.441×10 ⁻⁵	-49.360	-189.019	8.742	0.02441	0.07	[22]
PEG8000 +			0.00-0.37								
Na ₂ SO ₄ + H ₂ O	6400	20	0.00-0.09	0.022	0.101	-316.787	-893.658	2.370	0.5625	0.008	[22]
PEG1000 +			0.00-0.35								
Na ₂ CO ₃ + H ₂ O	980	20	0.00-0.08	-2.135	0.101	-52.992	-249.764	13.450	0.5625	0.05	[22]
PEG8000 +			0.00-0.36								
Na ₂ CO ₃ + H ₂ O	6400	20	0.00-0.06	-0.989	0.402	-340.100	-982.835	4.856	2.250	0.009	[22]
PEG4000 +			0.00-0.32								
KH ₂ PO ₄ + H ₂ O	3800	24	0.00-0.08	6.453	0.024	46.498	-760.84	-23.542	0.1407	0.03	[21]
PEG10000 +			0.00-0.32								
KH ₂ PO ₄ + H ₂ O	9000	24	0.00-0.11	0.025	0.101	-698.92	-1582.00	-1.014	0.5625	0.05	[21]

Table 2. Continued

PEG4000 +			0.00-0.30								
K ₂ HPO ₄ + H ₂ O	3800	24	0.00-0.06	0.092	0.402	-747.073	-827.368	-2.034	2.250	0.03	[21]
PEG10000 +			0.00-0.37								
K ₂ HPO ₄ + H ₂ O	9000	30	0.00-0.14	-7.214	-83.26	-5008.000	-1844.00	-667.167	2.343	0.04	[21]
PPG425 +											
(NH ₄) ₂ SO ₄ +			0.00-0.69								
H ₂ O	404	36	0.00-0.19	1.539	0.025	-9.821	23.174	-5.913	0.1406	0.13	[23]
PPG425 +			0.00-0.43								
MgSO ₄ + H ₂ O	404	32	0.00-0.14	1.462	-1.446×10 ⁻⁴	-8.518	-0.672	0.030	48.000	0.03	[24]
PPG425 +			0.00-0.60								
Na ₂ SO ₄ + H ₂ O	404	40	0.00-0.16	-0.009096	5.741	-69.822	-69.281	-3.535	2.250	0.07	[23]

Table 3. Comparison of Absolute Average Relative Deviations (100.AARD) of Different Local Composition Models in the Correlation of the Solvent Activity (a_m) of Ternary Aqueous Polymer + Electrolyte Solutions at 298.15 K

System	Polymer M_n	N	Concentration Range (w/w)	100.AARD NRTL (6) ^a	100.AARD Wilson (6) ^a	100.AARD mNRTL (6) ^a	100.AARD mWilson (6) ^a	100.AARD TNRF- mNRTL (6) ^a	Source data
PEG1000 +			0.00-0.40						
(NH ₄) ₂ SO ₄ + H ₂ O	1000	20	0.00-0.15	0.15	0.12	0.13	0.12	0.05	[19]
PEG4000 +			0.00-0.40						
(NH ₄) ₂ SO ₄ + H ₂ O	3800	20	0.00-0.15	0.05	0.05	0.05	0.05	0.02	[19]
PEG6000 +			0.00-0.41						
(NH ₄) ₂ SO ₄ + H ₂ O	6000	24	0.00-0.10	0.12	0.12	0.11	0.11	0.01	[20]
PEG10000 +			0.00-0.30						
(NH ₄) ₂ SO ₄ + H ₂ O	9000	15	0.00-0.04	0.04	0.04	0.04	0.04	0.02	[21]
PEG1000 +			0.00-0.34						
MgSO ₄ + H ₂ O	1000	15	0.00-0.15	0.20	0.15	0.18	0.16	0.05	[19]
PEG4000 +			0.00-0.34						
MgSO ₄ + H ₂ O	3800	15	0.00-0.11	0.14	0.09	0.11	0.11	0.04	[19]
PEG8000 +			0.00-0.31						
MgSO ₄ + H ₂ O	6400	20	0.00-0.09	0.10	0.08	0.09	0.08	0.02	[22]
PEG10000 +			0.00-0.16						
MgSO ₄ + H ₂ O	9000	10	0.00-0.12	0.22	0.22	0.22	0.21	0.01	[21]

Table 3. Continued

PEG1000 + Na ₂ SO ₄ +			0.00-0.37						
H ₂ O	980	20	0.00-0.12	0.08	0.07	0.08	0.08	0.07	[22]
PEG8000 + Na ₂ SO ₄ +			0.00-0.37						
H ₂ O	6400	20	0.00-0.09	0.10	0.07	0.07	0.07	0.008	[22]
PEG1000 + Na ₂ CO ₃ +			0.00-0.35						
H ₂ O	980	20	0.00-0.08	0.07	0.07	0.08	0.07	0.05	[22]
PEG8000 + Na ₂ CO ₃ +			0.00-0.36						
H ₂ O	6400	20	0.00-0.06	0.08	0.06	0.06	0.08	0.009	[22]
PEG4000 + KH ₂ PO ₄ +			0.00-0.32						
H ₂ O	3800	24	0.00-0.08	0.06	0.07	0.07	0.07	0.03	[21]
PEG10000 + KH ₂ PO ₄			0.00-0.32						
+ H ₂ O	9000	24	0.00-0.11	0.21	0.21	0.22	0.21	0.05	[21]
PEG4000 + K ₂ HPO ₄ +			0.00-0.30						
H ₂ O	3800	24	0.00-0.06	0.04	0.04	0.05	0.04	0.03	[21]
PEG10000 + K ₂ HPO ₄			0.00-0.37						
+ H ₂ O	9000	30	0.00-0.14	0.19	0.22	0.24	0.18	0.04	[21]
PPG425 + (NH ₄) ₂ SO ₄			0.00-0.69						
+ H ₂ O	404	36	0.00-0.19	0.20	0.14	0.14	0.14	0.13	[23]
PPG425 + MgSO ₄ +			0.00-0.43						
H ₂ O	404	32	0.00-0.14	0.18	0.12	0.15	0.11	0.03	[24]
PPG425 + Na ₂ SO ₄ +			0.00-0.60						
H ₂ O	404	40	0.00-0.16	0.21	0.14	0.16	0.16	0.07	[23]
Overall				0.13	0.11	0.12	0.11	0.04 (0.16) ^b	

^aThe number of model adjustable parameters have been given in the parentheses. ^bOverall 100.AARD of TNRF-mNRTL model with two adjustable parameters has been given in the parenthesis.

parameters of this model (λ_{Es} and λ_{sE}) along with the absolute average relative deviations (AARD) are collected in Table 1. Parameters of λ_{Em} and λ_{mE} were obtained from fitting the solvent activity of binary aqueous electrolyte solutions with TNRF-mNRTL model. Parameters of λ_{sm} and λ_{ms} were also obtained from correlating the solvent activity of binary aqueous polymer solutions with proposed model. These parameters are also reported in Table 1. As reported

in this table, The performance of the proposed model with only two parameters is good in correlating the solvent activity data of the ternary aqueous solutions containing the polymer with different molar masses and also multivalent electrolytes in a variety of concentration ranges. However, for PEG1000 + MgSO₄ + H₂O, PEG8000 + MgSO₄ + H₂O and PPG425 + MgSO₄ + H₂O systems rather high deviations were obtained. Applicability of TNRF-mNRTL

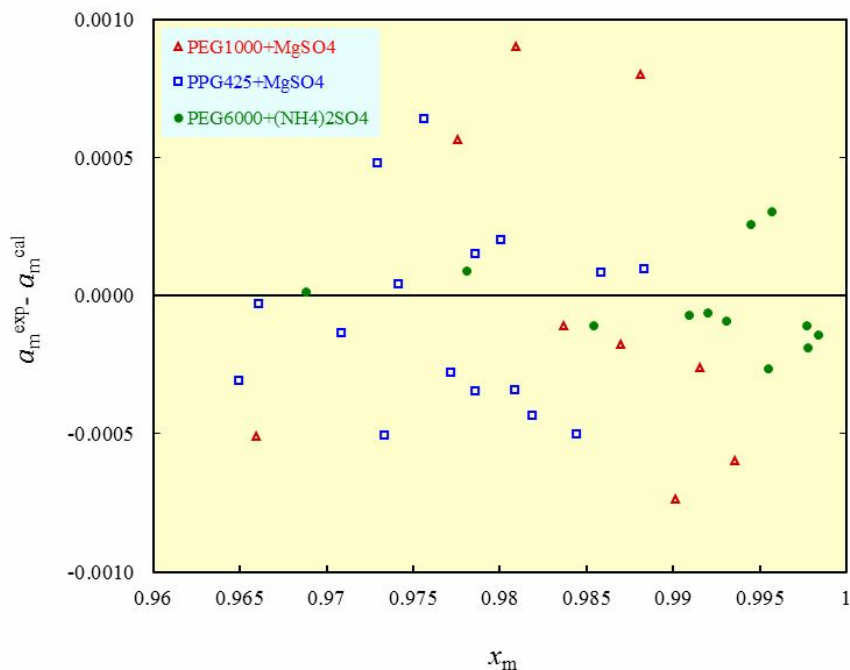


Fig. 2. Difference between solvent activity data (a_m) and calculated values with TNRF-mNRTL model plotted against solvent mole fraction (x_m) for different ternary aqueous polymer + electrolyte solutions.

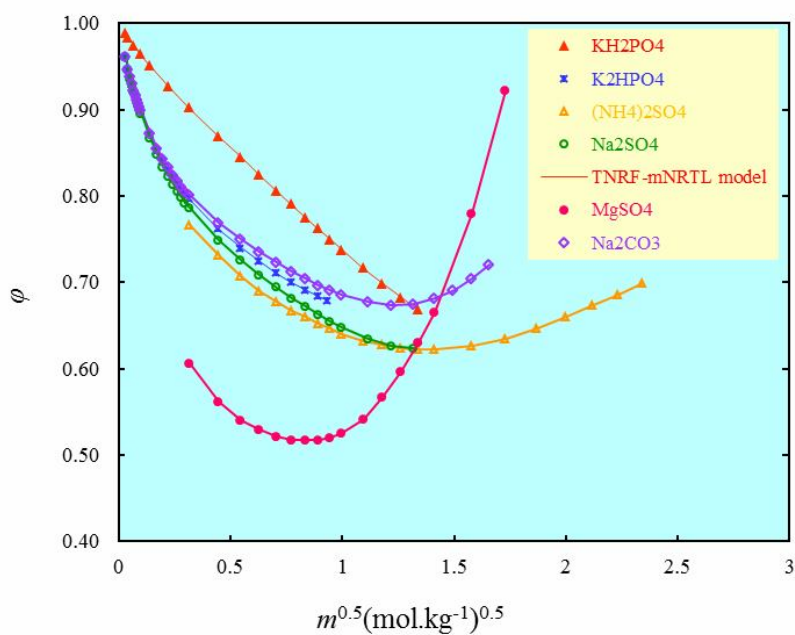


Fig. 3. Osmotic coefficient data (ϕ) and calculated values by TNRF-mNRTL model plotted against molality of solution, $m^{0.5}$, for different binary aqueous electrolyte solutions at 298.15.

model in correlating the solvent activity of the ternary aqueous polymer + electrolyte solutions has also been compared with other local composition models available in the literature for these systems (ternary NRTL [7], ternary Wilson [8], ternary modified NRTL [9] and ternary modified Wilson [10] models). Close examination of literature indicates that these models with six adjustable parameters have good performance; therefore, in this work the performance of the proposed model with six adjustable parameters in fitting the solvent activity values has also been tested. The obtained results have been reported in Table 2. The AARD values for the solvent activity obtained from different models with six parameters are reported in Table 3. The overall AARD values are also given in this table. On the basis of the overall AARD values, we conclude that the performance of TNRF-mNRTL model in the correlation of the solvent activity values is very better than the other local composition models. Table 3 also shows that the fitting quality of the new model with two adjustable parameters is also comparable with that of other local composition models with six parameters.

To clarify the performance of TNRF-mNRTL model, the difference between solvent activity data and calculated values has been plotted in Fig. 2 for different aqueous ternary solutions of PEG6000 + (NH₄)₂SO₄, PEG1000 + MgSO₄, and PPG425 + MgSO₄ as examples; for other systems similar results were also obtained. The osmotic coefficient data (φ) of binary aqueous electrolyte solutions have also been calculated from the solvent activity values using the relation of $\varphi = -\frac{(\ln a_m)}{vmM_m}$ [13], in which m is the

molality of solution. Therefore, to see the reliability of the proposed model in fitting the osmotic coefficient data of binary electrolyte solutions, the experimental and calculated φ values with TNRF-mNRTL model have also been plotted in Fig. 3 for the aqueous solutions of (NH₄)₂SO₄, MgSO₄, Na₂SO₄, Na₂CO₃, KH₂PO₄ and K₂HPO₄ at 298.15 K. From these figures one can conclude that the performance of the proposed model in correlating the solvent activity of ternary solutions and also osmotic coefficient values of the aqueous electrolyte solutions is very good.

CONCLUSIONS

A new local composition model with considering the four types of cell with central molecules of solvent, anion, cation and polymer segment has been developed for representing the excess Gibbs energy of solutions containing electrolyte and polymer. The corresponding activity coefficient equation has been derived from the proposed model. This model is applied to correlate the solvent activity of ternary solutions of polymer + electrolyte + water and binary solutions of polymer + water and electrolyte + water. Fitting quality of the proposed model (TNRF-mNRTL) for the solvent activity of ternary polymer + electrolyte + water solutions has been compared with the ternary NRTL, ternary Wilson, ternary modified NRTL and ternary modified Wilson models, and it was found that the performance of the proposed model in the correlation of the solvent activity values is much better than the other local composition models with same numbers of the adjustable parameters. In addition, it was found that the fitting quality of new model with only two adjustable parameters is comparable with that of other local composition models with six adjustable parameters.

REFERENCES

- [1] Albertsson, P. A., Partition of proteins in liquid polymer-polymer two-phase systems. *Nature* **1958**, *182*, 709-711, DOI: 13590079.
- [2] Rogers, R. D.; Zhang, J., New technology for ion separations polyethylene glycol based-aqueous biphasic system and aqueous biphasic extraction chromatography. In: Marinsky, J. A.; Marcus, Y., (Eds.), Ion Exchange and Solvent Extraction. Marcel Dekker, New York, 1997, 13, 141-193 (Chapter 4).
- [3] Willauer, H. D.; Huddleston, J. G.; Rogers, R. D., Solute partitioning in aqueous biphasic systems composed of polyethylene glycol and salt: The Partitioning of small neutral organic species. *Ind. Eng. Chem. Res.* **2002**, *41*, 1892-1904, DOI: 10.1021/ie010598z.
- [4] Albertsson, P. -A.; Johansson, G.; Tjerneld, F., Separation Processes in Biotechnology. Marcel Dekker, New York, 1990.

- [5] Kabiri-Badr, M.; Cabezas, H., A thermodynamic model for the phase behavior of salt-polymer aqueous two-phase systems. *Fluid Phase Equilib.* **1996**, *115*, 39-58, DOI: 10.1016/0378-3812(95)02831-5.
- [6] Wu, Y. T.; Lin, D. Q.; Zhu, Z. Q.; Mei, L. H., Prediction of liquid-liquid equilibria of polymer-salt aqueous two-phase systems by a modified Pitzer's virial equation. *Fluid Phase Equilib.* **1996**, *124*, 67-79, DOI: 10.1016/S0378-3812(96)03066-X.
- [7] Zafarani-Moattar, M. T.; Sadeghi, R., Measurement and correlation of liquid-liquid equilibria of the aqueous two-phase system polyvinylpyrrolidone-sodium dihydrogen phosphate. *Fluid Phase Equilib.* **2002**, *203*, 177-191, DOI: 10.1016/S0378-3812(02)00179-6.
- [8] Sadeghi, R., A modified Wilson model for the calculation of vapour + liquid equilibrium of aqueous polymer + salt solutions. *J. Chem. Thermodyn.* **2005**, *37*, 323-329, DOI: 10.1016/j.jct.2004.09.016.
- [9] Sadeghi, R., A modified segment-based nonrandom two-liquid model for the calculation of vapor-liquid equilibrium of aqueous polymer-salt solutions. *Chem. Eng. Sci.* **2006**, *61*, 7786-7794, DOI: 10.1016/j.ces.2006.09.031.
- [10] Sadeghi, R., Representation of vapor-liquid equilibria of aqueous polymer-salt solutions by a new modified segment-based Wilson model. *Calphad* **2007**, *31*, 164-172, DOI: 10.1016/j.calphad.2007.01.001.
- [11] Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B., Local composition model for excess Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982**, *28*, 588-596, DOI: 10.1002/aic.690280410.
- [12] Flory, P. J., Thermodynamics of high polymer solutions. *J. Chem. Phys.* **1941**, *9*, 660-661, DOI: 10.1063/1.1750971.
- [13] Pitzer, K. S., Activity coefficients in electrolyte solutions. 2nd ed. CRC Press, Inc. 1991.
- [14] Chen, C. C., A segment-based local composition model for the Gibbs energy of polymer solutions. *Fluid Phase Equilib.* **1993**, *83*, 301-312, DOI: 10.1016/0378-3812(93)87033-W.
- [15] Haghtalab, A.; Vera, J. H., A nonrandom factor model for the excess Gibbs energy of electrolyte solutions. *AIChE J.* **1988**, *34*, 803-813, DOI: 10.1002/aic.690340510.
- [16] Zafarani-Moattar, M. T.; Majdan-Cegincara, R., New local composition model for modeling of thermodynamic and transport properties of binary aqueous electrolyte solutions. *Calphad* **2011**, *35*, 109-132, DOI: 10.1016/j.calphad.2010.12.005.
- [17] Zafarani-Moattar, M. T.; Majdan-Cegincara, R., New excess Gibbs energy equation for modeling the thermodynamic and transport properties of polymer solutions and nanofluids at different temperatures. *Ind. Eng. Chem. Res.* **2011**, *50*, 8245-8262, DOI: 10.1021/ie200003c.
- [18] Simonson, J. M.; Pitzer, K. S., Thermodynamics of multicomponent, miscible ionic systems: the system lithium nitrate-potassium nitrate-water. *J. Phys. Chem.* **1986**, *90*, 3009-3013, DOI: 10.1021/j100404a043.
- [19] Lin, D. -Q.; Mei, L. -H.; Zhu, Z. -Q.; Han, Z. -X., An improved isopiestic method for measurement of water activities in aqueous polymer and salt solutions. *Fluid Phase Equilib.* **1996**, *118*, 241-248, DOI: 10.1016/0378-3812(95)02853-6.
- [20] Salabat, A.; Nasirzadeh, K., Measurement and prediction of water activity in PEG+(NH₄)₂SO₄+H₂O systems using polymer scaling laws. *J. Mole. Liq.* **2003**, *103-104*, 349-358, DOI: 10.1016/S0167-7322(02)00153-8.
- [21] Lin, D. -Q.; Zhu, Z. -Q.; Mei, L. -H.; Yang, L. -R., Isopiestic determination of the water activities of poly(ethylene glycol) + salt+ water systems at 25 °C. *J. Chem. Eng. Data* **1996**, *41*, 1040-1042, DOI: 10.1021/je960065a.
- [22] Ochs, L. R. Kabiri-Badr, M.; Cabezas, H., An improved isopiestic method to determine activities in multicomponent mixtures. *AIChE J.* **1990**, *36*, 1908-1912, DOI: 10.1002/aic.690361216.
- [23] Salabat, A.; Dashti, H.; Nasirzadeh, K., Measurement and correlation of water activities and refractive indices for the systems PPG425 + (NH₄)₂SO₄ + H₂O and PPG425 + Na₂SO₄ + H₂O at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 980-982, DOI: 10.1021/je034291d.
- [24] Ninni, L.; Camargo, M. S.; Meirelles, A. J., water

- activity in poly (ethylene glycol) aqueous solutions. *Thermochimica Acta* **1999**, 328, 169-176, DOI: 10.1016/S0040-6031(98)00638-8.
- [25] Zafarani-Moattar, M. T.; Salabat, A., Measurement and correlation of viscosities, densities, and water activities for the system poly (propylene glycol)+ MgSO₄ + H₂O at 25 °C. *J. Solu. Chem.* **1998**, 27, 663-673, DOI: 10.1023/A:1022650025229.
- [26] Robinson, R. A.; Stokes, R. H., *Electrolyte Solutions*. 2nd ed. Butterworths, London, 1965.
- [27] Goldberg, R., Evaluated activity and osmotic coefficients for aqueous solutions: thirty-six uni-bivalent electrolytes. *J. Phys. Chem. Ref. Data* **1981**, 10, 671-704, DOI: 10.1063/1.555646.
- [28] Hamer, W. J.; Wu, Y. C., Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, 1, 1047-1100, DOI: 10.1063/1.3253108.